Aqueous Complexation Reactions Governing the Rate and Extent of Biogeochemical U(VI) Reduction

Scott C. Brooks*[1], Wenming Dong[1], Sue Carroll[1],

James K. Fredrickson[2], Kenneth M. Kemner[3], Shelly Kelly[3]

Collaborators: Kent Orlandini[3], John Zachara[2]

[1] ***Oak Ridge National Laboratory***

[2] ***Pacific Northwest National Laboratory***

[3] ***Argonne National Laboratory***

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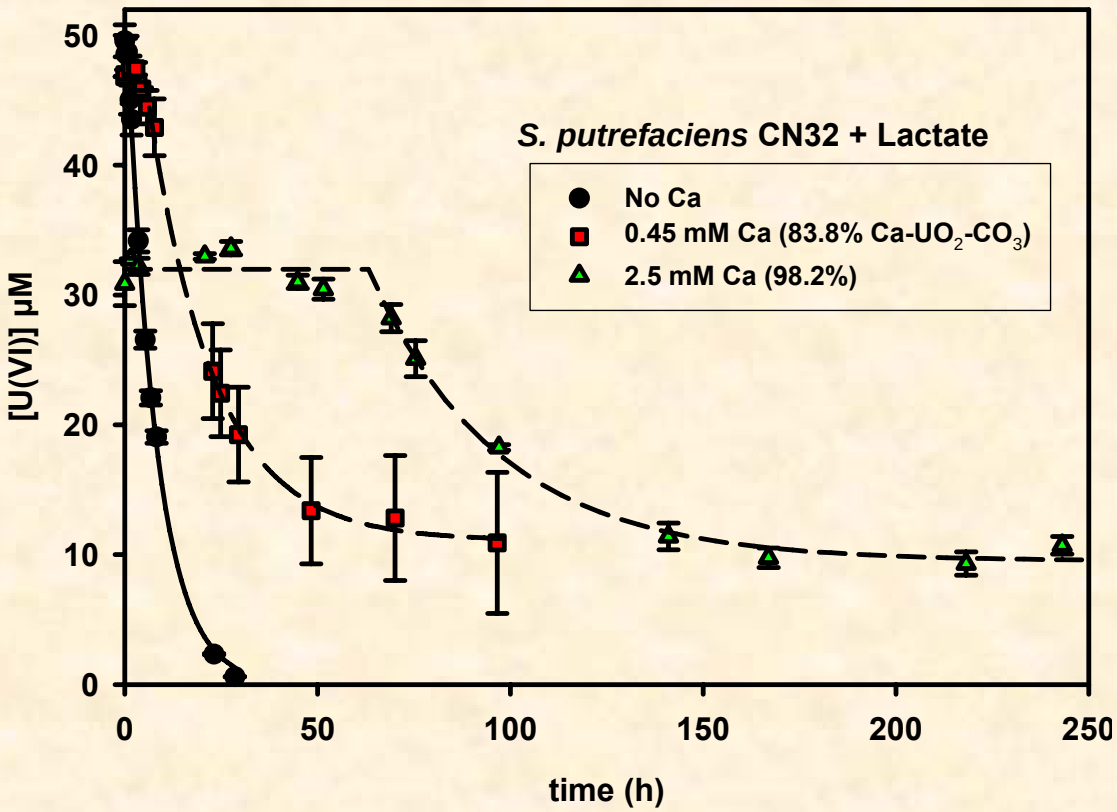
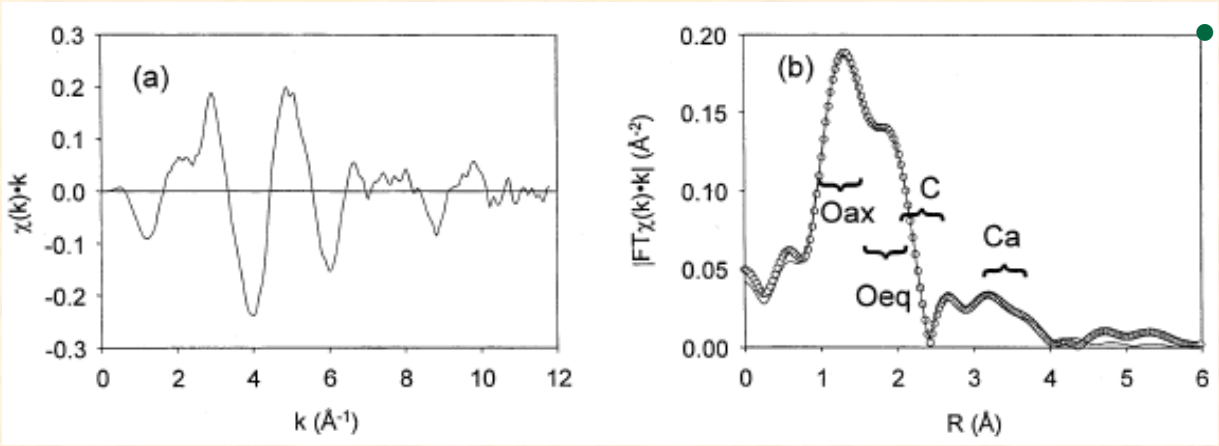




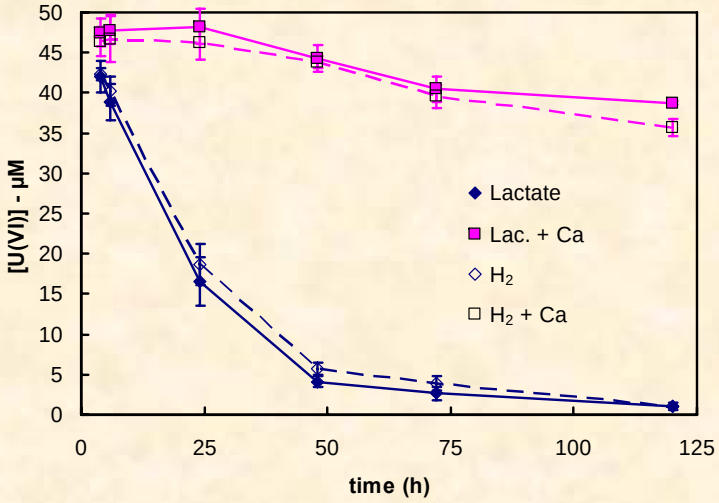
The effect of Ca did not depend on:

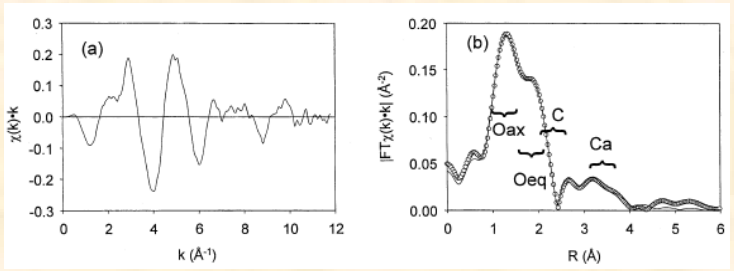
- **Bacterial strain:**
  - ***S. algae* BrY**
  - ***S. putrefaciens* SN32**
  - ***Desulfovibrio desulfuricans***
  - ***Geobacter sulfurreducens***
  - ***G. metallireducens* GS-15**
- **Antecedent culture conditions: aerobic, anaerobic.**
- **Electron donor: Lactate, Acetate, H_2.**

The effect of Ca did depend on:

- **Electron acceptor:**
  - ✓ **U(VI)**
  - × **Tc(VII)**
  - × **Fumarate**
  - × **Co(III)EDTA**

(Brooks et al., 2003)





Link between U(VI) speciation and direct bacterial reduction

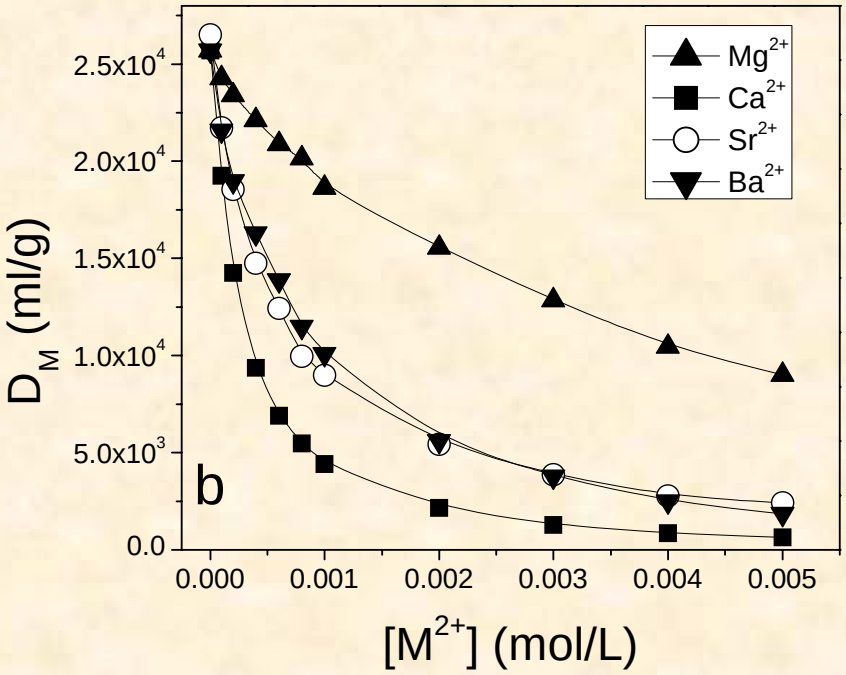
Implications for Biogeochemical U(VI) Reduction?

Ternary Complex Formation:
Other M-UO_2-CO_3 complexes exist. Their influence on rate and extent of bacterial U(VI) reduction will be a function of their net charge and stability.

Abiotic Reduction:
Indirect reduction of U(VI) (e.g., surface associated Fe(II)) is inhibited by formation of M-UO_2-CO_3 complexes. Effect proportional to stability constants.

Microbial Reduction:
Retardation of microbial metal reduction activity will be restricted to M-UO_2-CO_3 complexes (i.e., no effect on Fe(III) reduction).

Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) using an anion exchange method (Dong and Brooks, *in review*)



$$\frac{D_0}{D_M} - 1 = K_1[M^{2+}]_{aq} + K_2[M^{2+}]_{aq}^2$$

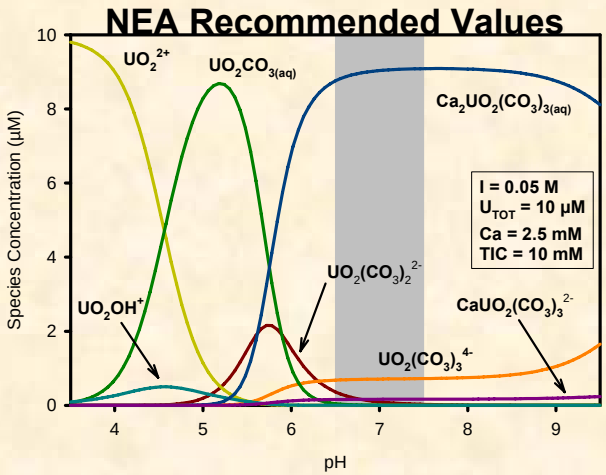
- **D_0, D_M, [M] measured by experiment.**
- **K_1 and K_2 determined from fit to data.**
- **F-test to determine the more appropriate model.**

Formation constants of the $MUO_2(CO_3)_3^{2-}$ (aq) and $M_2UO_2(CO_3)_3^0$ (aq) complexes.

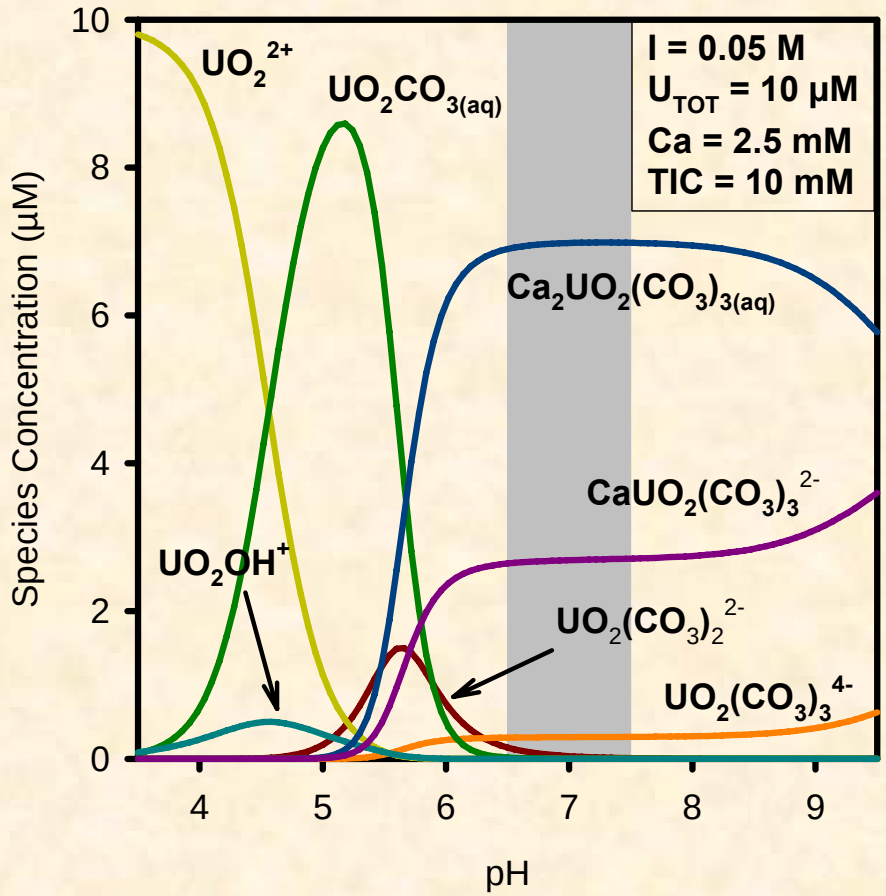
	$MUO_2(CO_3)_3^{2-}$	$M_2UO_2(CO_3)_3^0$	
M^{2+}	log β_{113} (I = 0)	log β_{213} (I = 0)	Reference
Mg^{2+}	26.11 ± 0.04	---[a]	This work
Ca^{2+}	27.18 ± 0.06	30.70 ± 0.05	This work
	---	29.41 ± 0.7[b]	Bernhard et al., 1996
	25.6 ± 0.25[b]	30.79 ± 0.25[b]	Bernhard et al., 2001
	---	29.8 ± 0.7[b]	Kalmykov and Choppin, 2000
Sr^{2+}	26.86 ± 0.04	---	This work
Ba^{2+}	26.68 ± 0.04	29.75 ± 0.07	This work

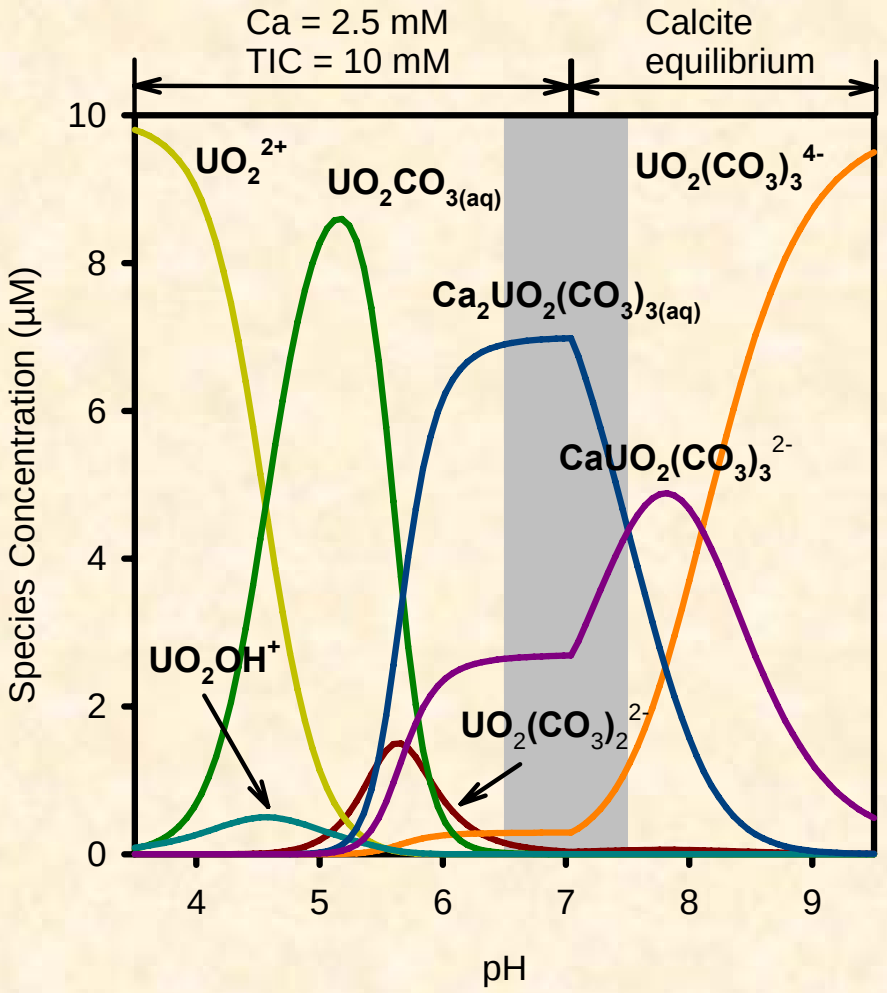
[a] = marginally significant at *P* = 0.0496 and therefore not accepted .

[b] = revised to reflect the new recommended value for formation constant of $UO_2(CO_3)_3^{4-}$ in Guillaumont et al. (2003).

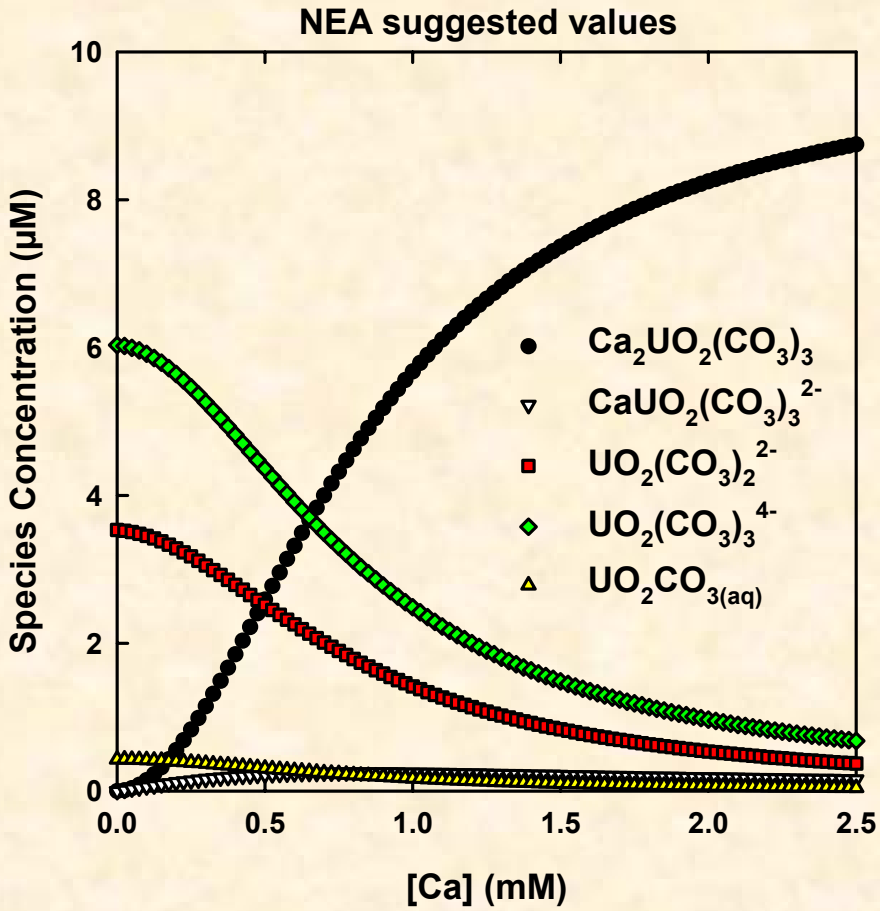


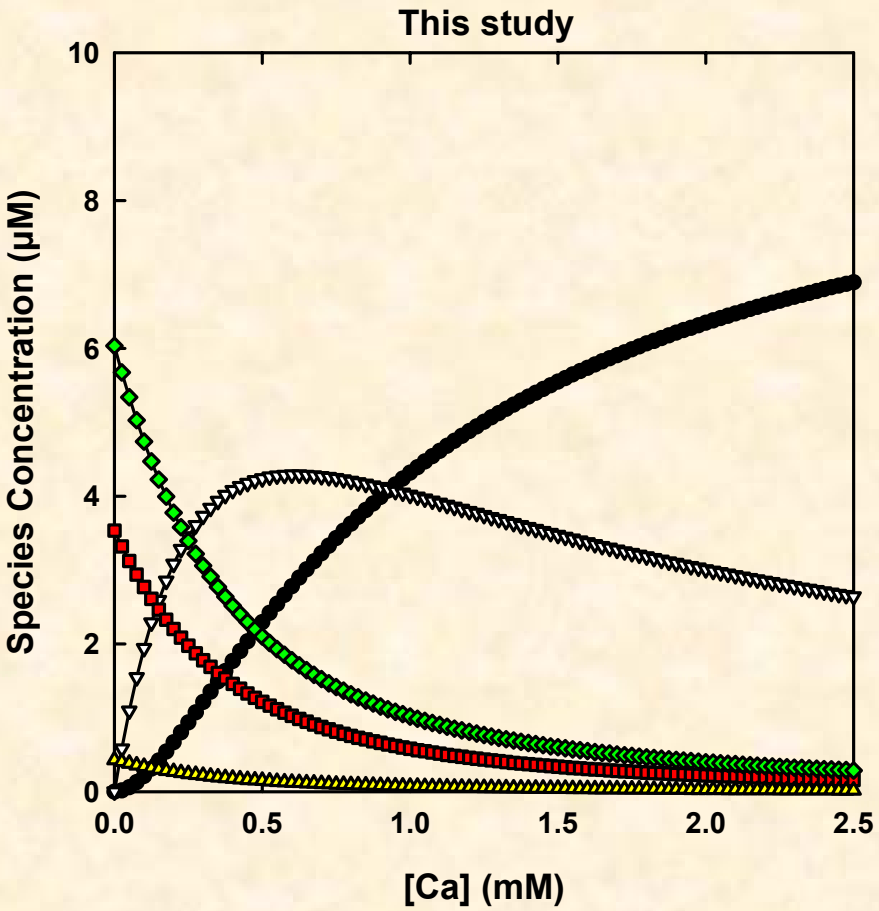
Implications of our estimated stability constants 1: Speciation as f(pH)





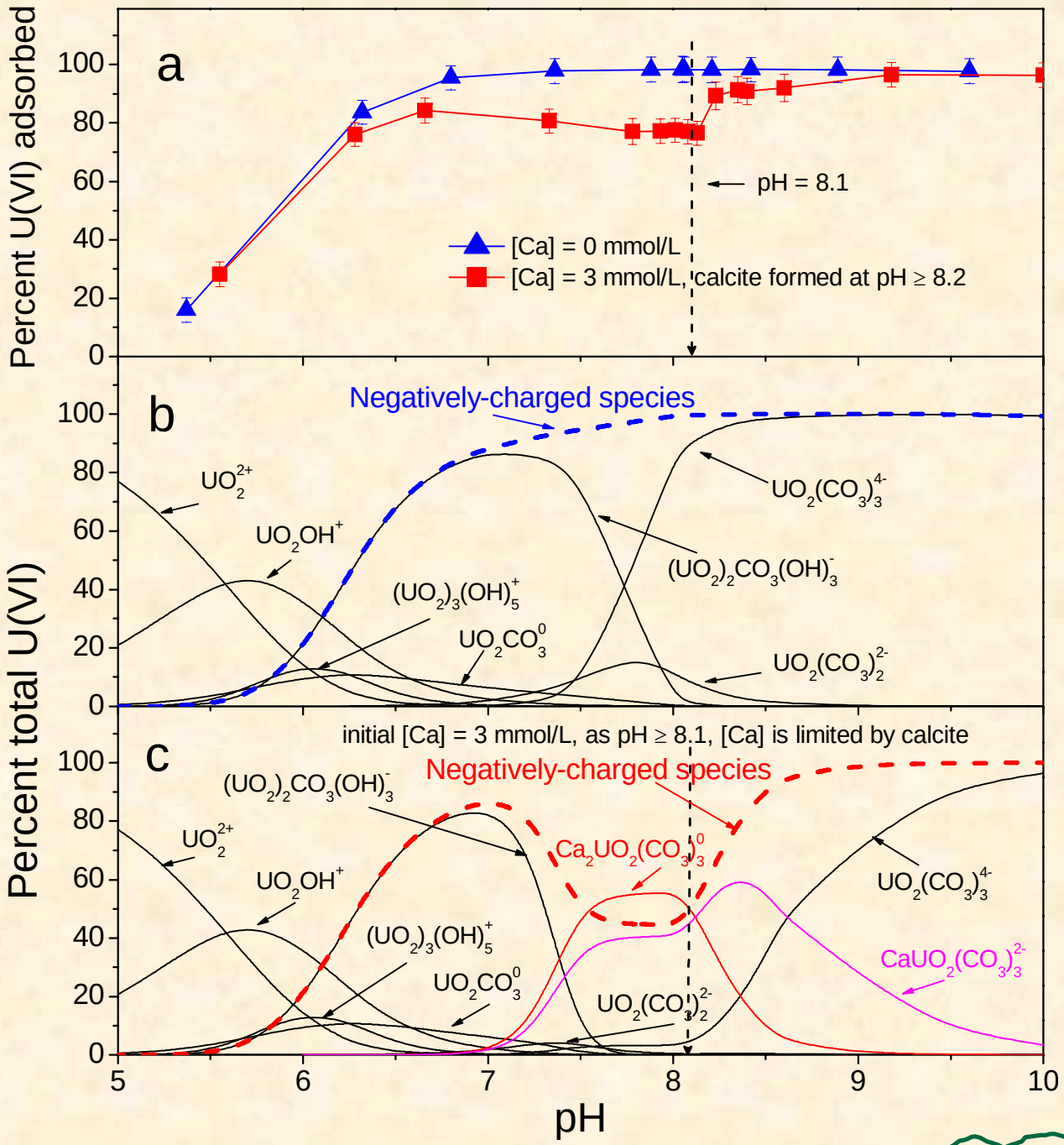
Implications of our estimated stability constants 2: Speciation as f([Ca])





I = 0.05; pH 8
TIC = 10 mM
U_{TOT} = 10 μM

U(VI) uptake by anion exchange resins inhibited by formation of neutral $Ca_2UO_2(CO_3)_3^0$



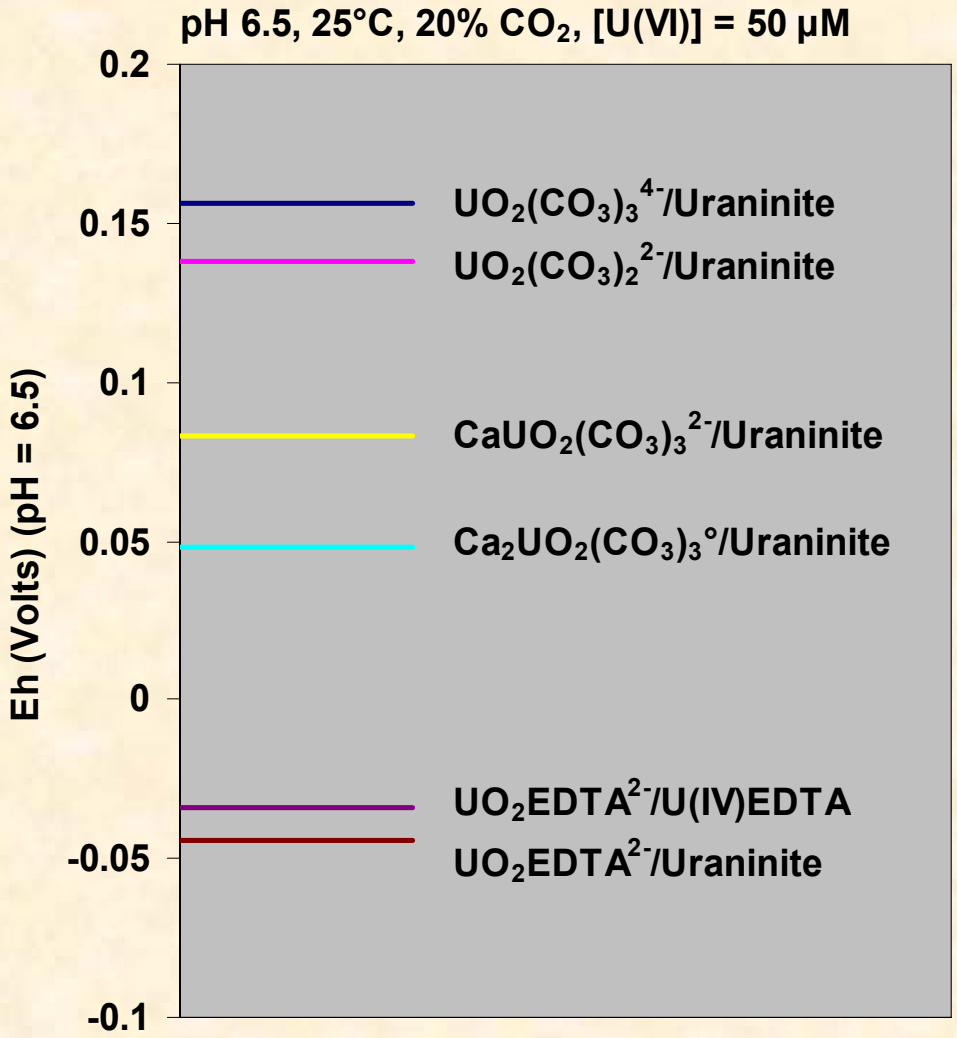
Summary 1:

- **Identified and quantified alkaline earth-uranyl-carbonate complexes.**
  - **Mg & Sr : $MUO_2(CO_3)_3^{2-}$ ****
  - **Ca & Ba : $MUO_2(CO_3)_3^{2-}$, $M_2UO_2(CO_3)_3^{0}$**
  - **Ca > Ba = Sr > Mg**
- **$CaUO_2(CO_3)_3^{2-}$ complex more important than previously suggested**
- **Decreased U partitioning to anion exchange resins correlate with predicted species distribution.**

Influence of EDTA and pH on Bioreduction of Uranium(VI) in the Presence of Calcium Ions (Dong et al., *in prep*)

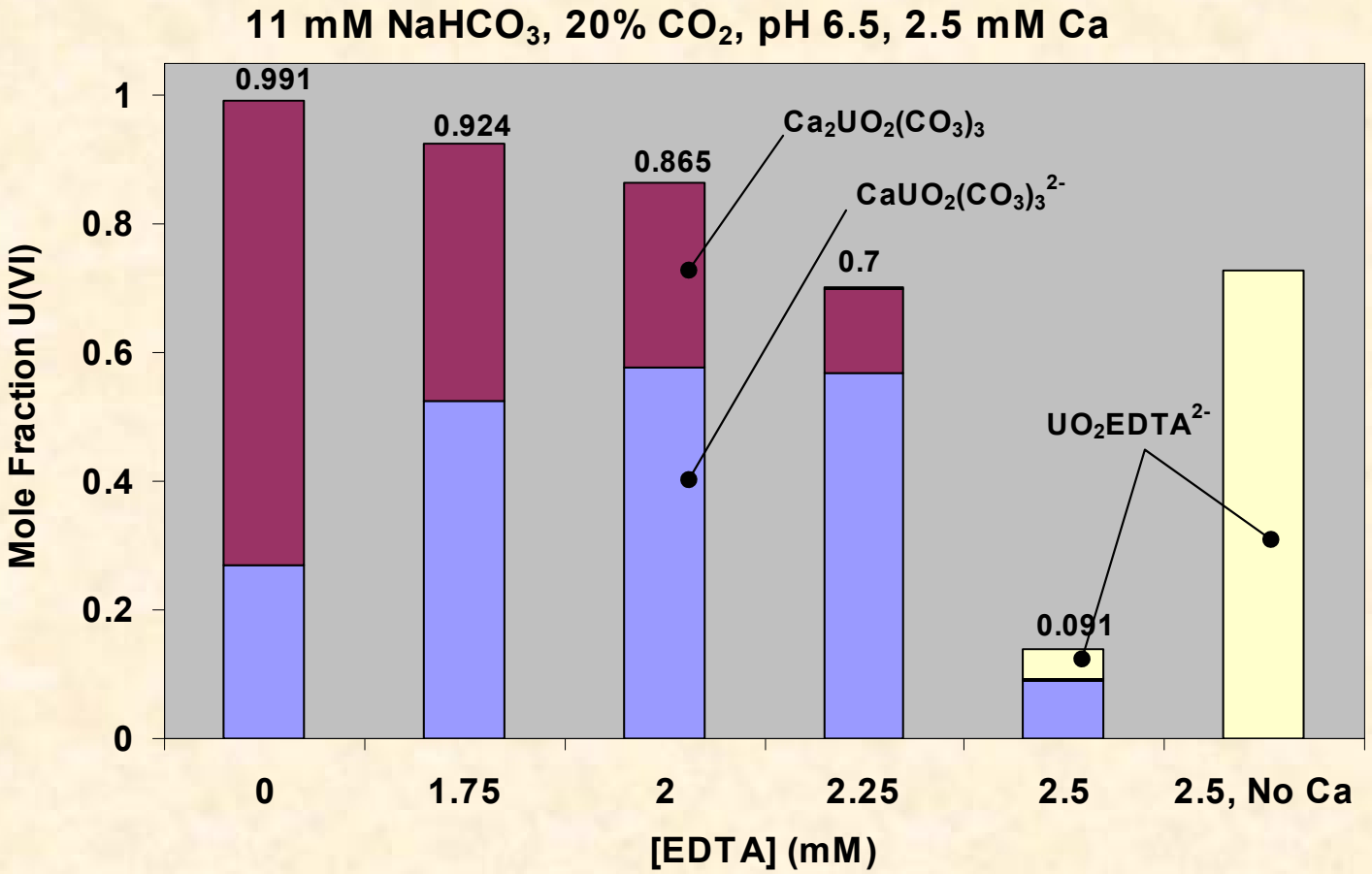
U(VI) Speciation : Implications for Bioreduction?

- **Thermodynamic considerations**
  - **U(VI) speciation affects reduction potential → energy available to microorganisms.**
- **Kinetic considerations**
  - **Synthesis of new cell components?**
  - **Speciation kinetics?**



Influence of EDTA and pH on Bioreduction of Uranium(VI) in the Presence of Calcium Ions (Dong et al., *in prep*)

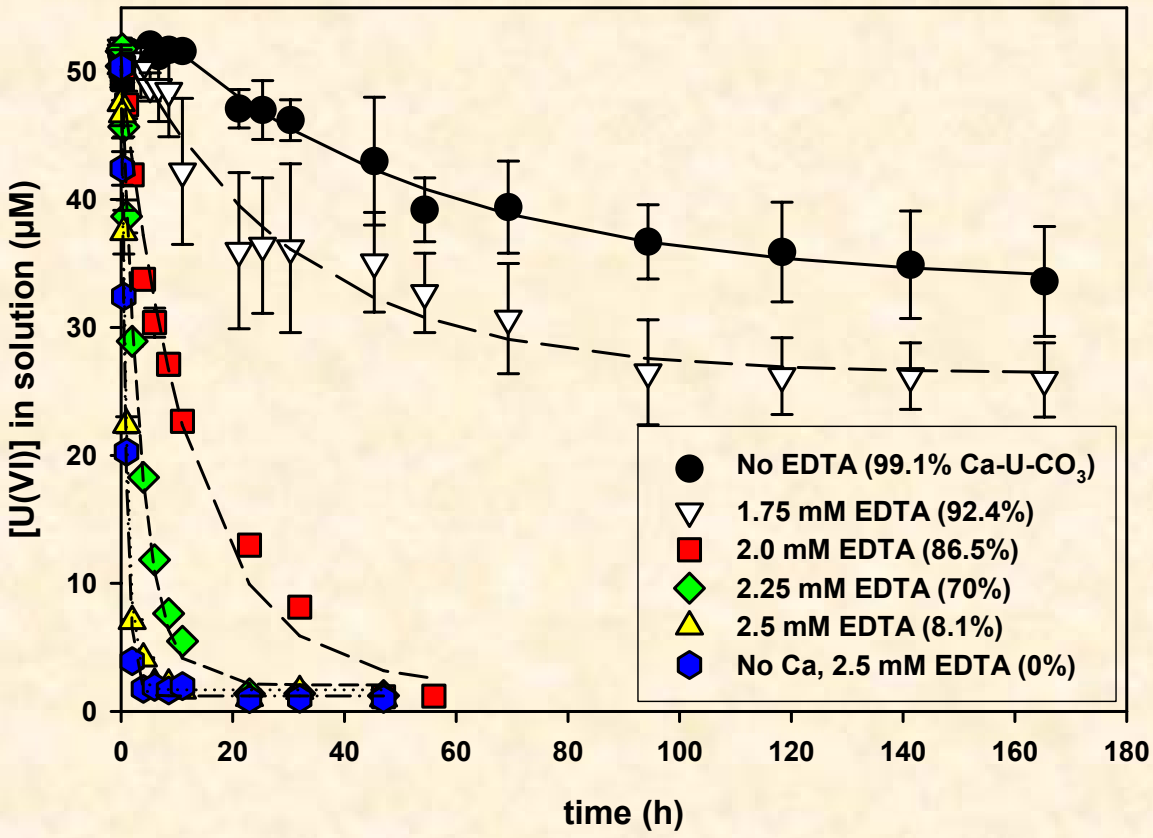
U(VI) Speciation as f([EDTA]) at pH 6.5



$UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$ constitute the balance of U(VI) species.

Influence of EDTA and pH on Bioreduction of Uranium(VI) in the Presence of Calcium Ions

- ***S. putrefaciens* CN32**
  - 11 mM $NaHCO_3$
  - 20% $CO_{2(g)}$
  - pH 6.5
  - 2.5 mM $CaCl_2$
- **Increasing [EDTA]:**
  - Decreased fraction Ca-U(VI)-CO_3 species.
  - Increased reduction rate.
  - Decreased lag phase.
  - More complete reduction.
  - Lines = pseudo 1° model
- **When EDTA present U_{TOT} constant in filtered fraction.**

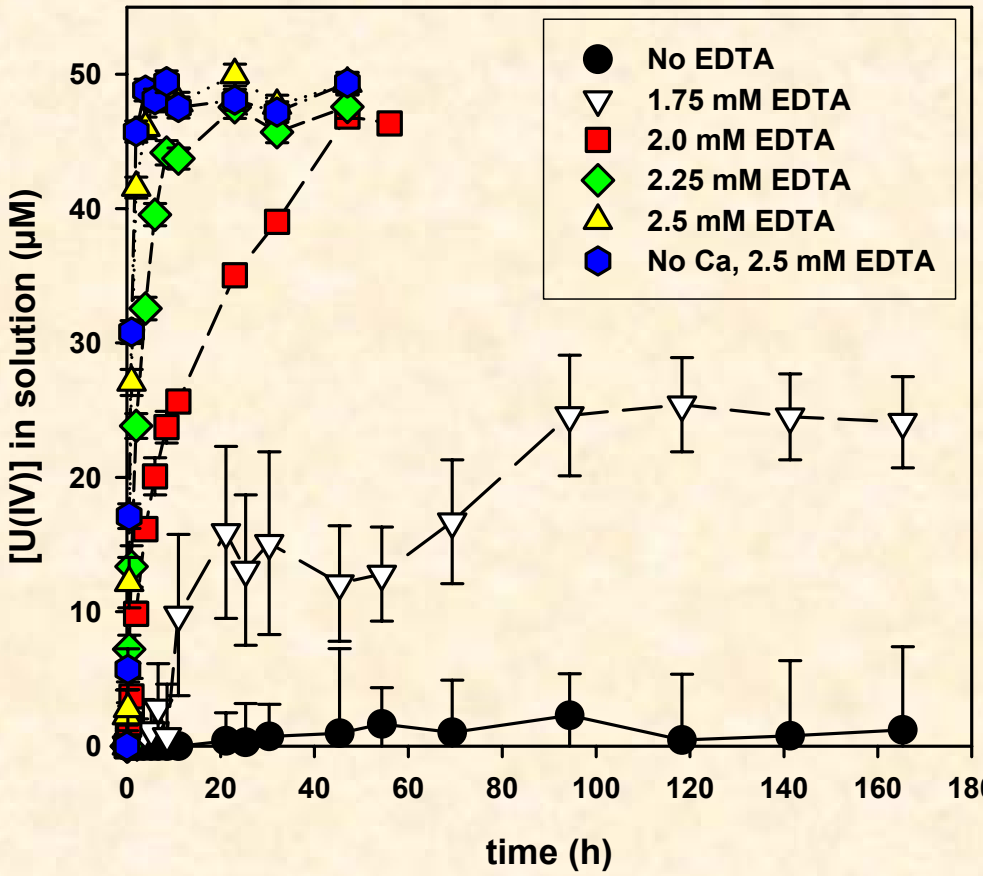


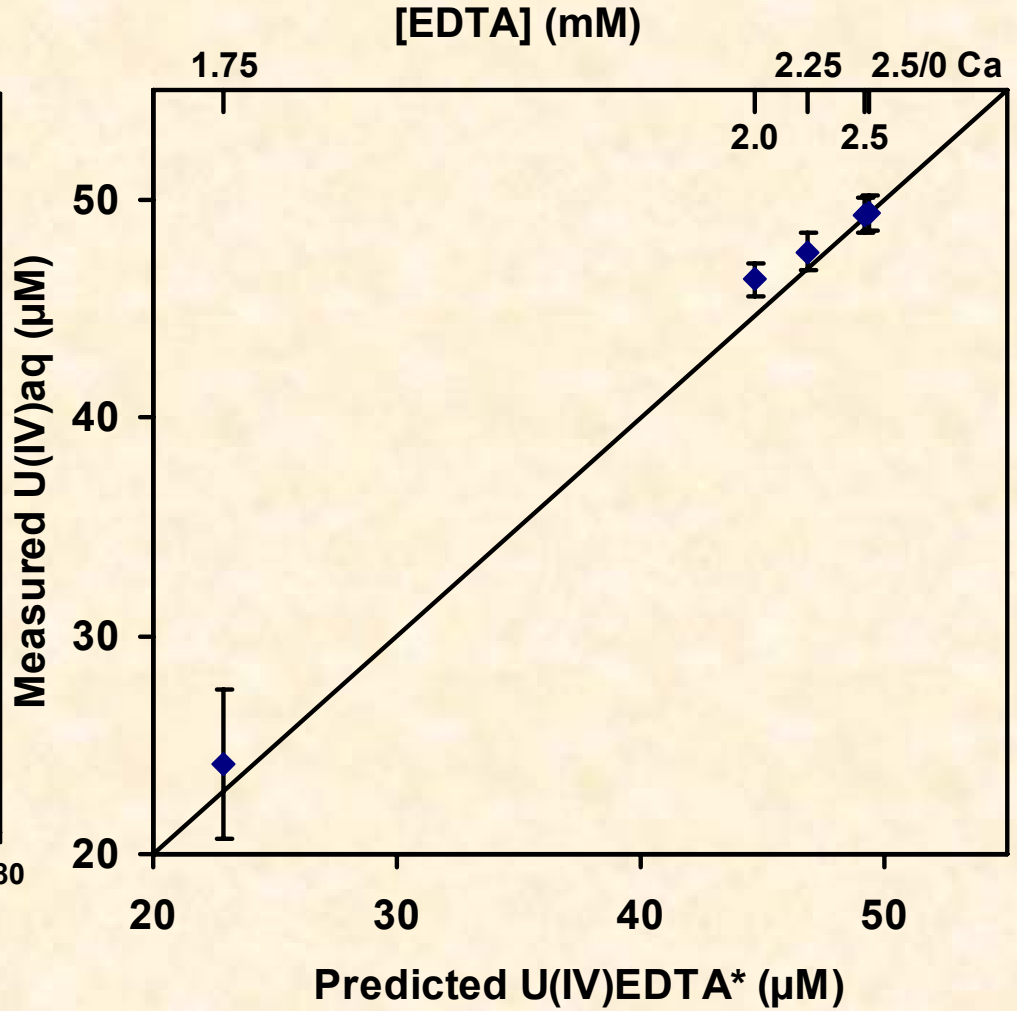
(Dong et al., in prep)

Fate of Biogenic U(IV) in presence of EDTA

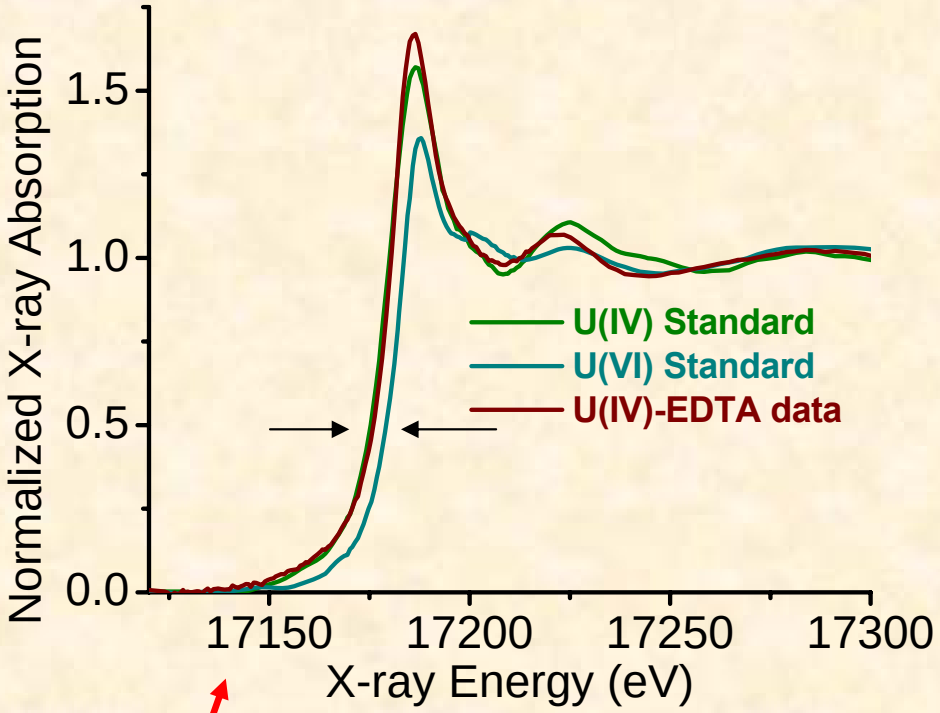
(*U(IV) in solution = U(IV) passing 0.2 µm pore size filter)

- **Suggests that a U(IV) solid phase with a higher solubility than $UO_{2,am}$ (Guillaumont et al., 2003) controlled [U(IV)].**
- **U(IV) stable in solution for at least 5 months (…and counting).**

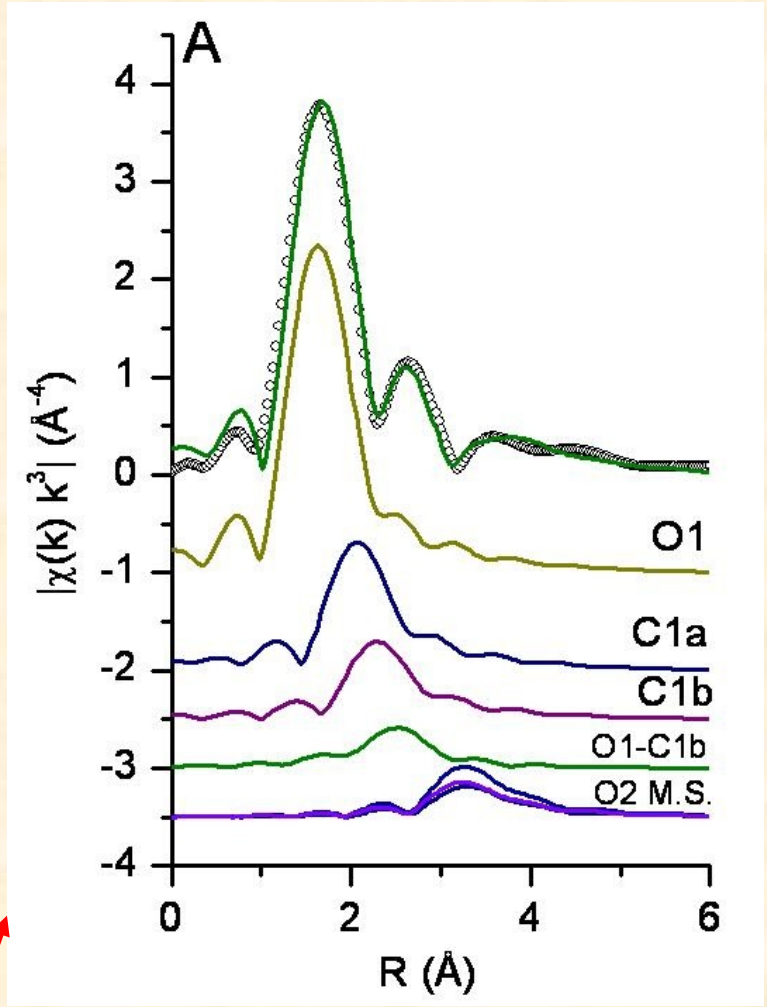




*assuming max solubility $UO_{2,am}$

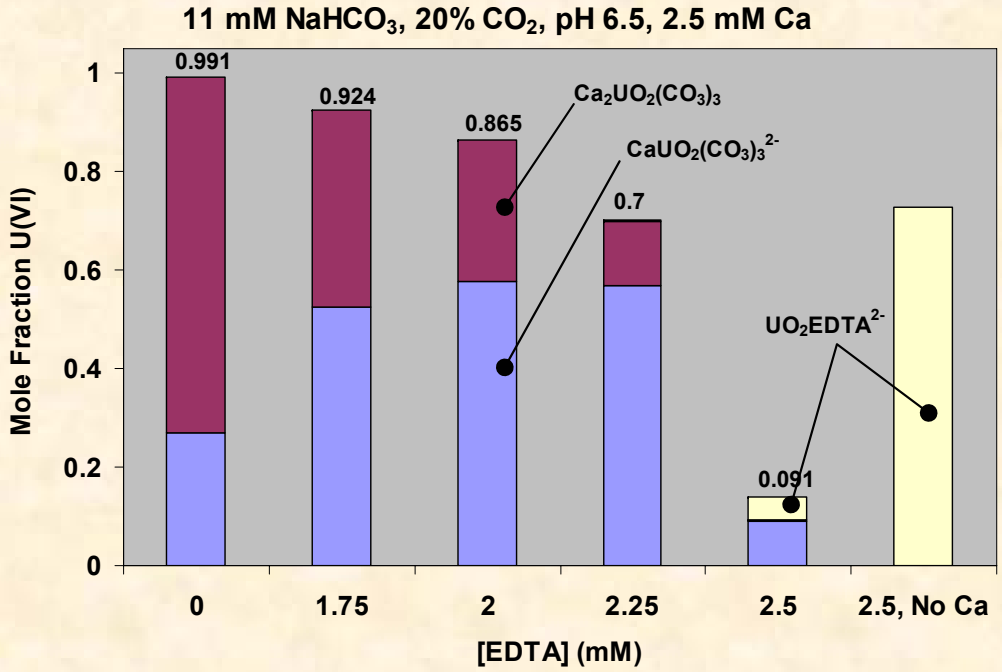


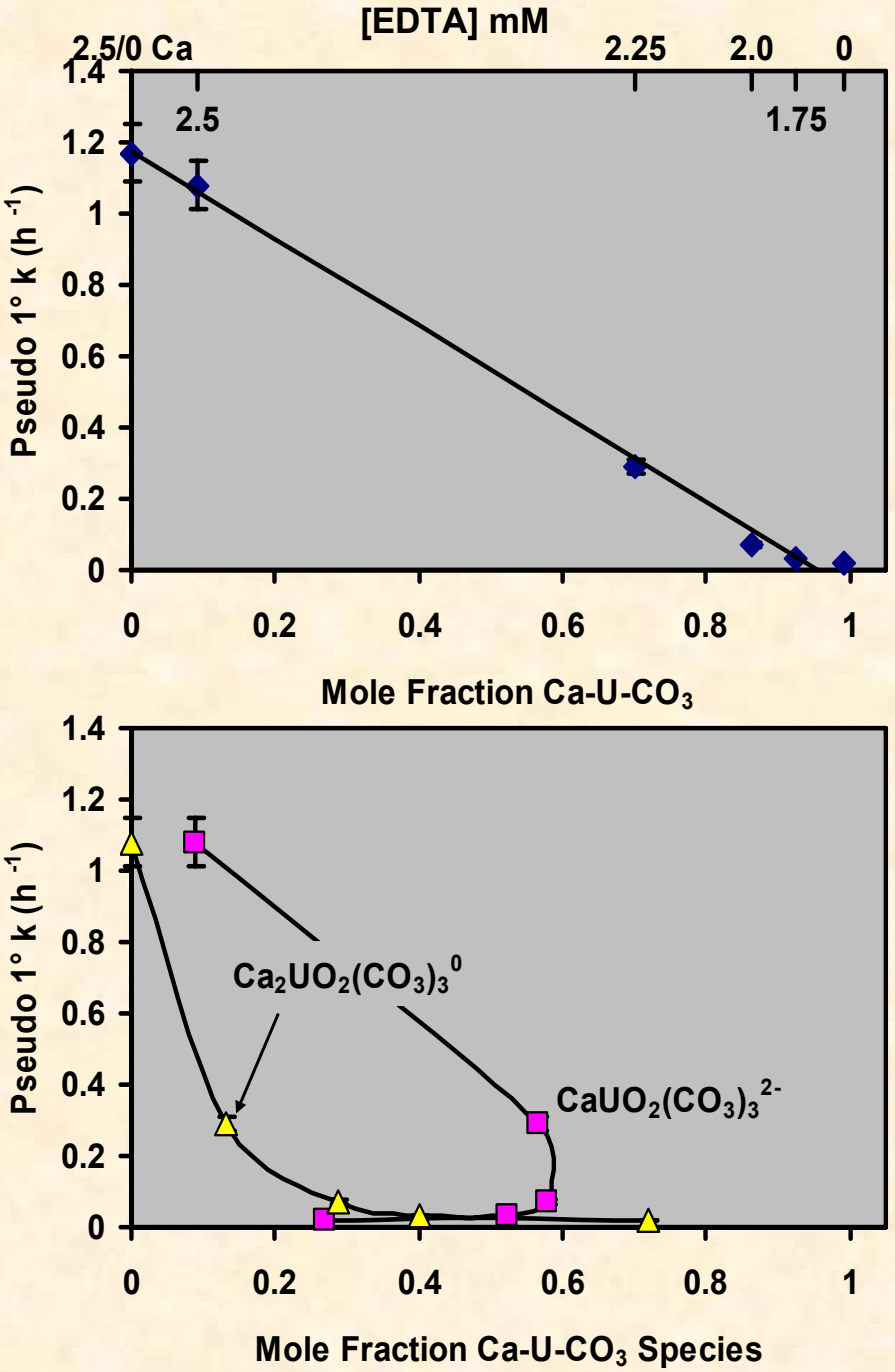
- **U-XANES verifies that the majority of the U in the sample is in the +4 valence state.**



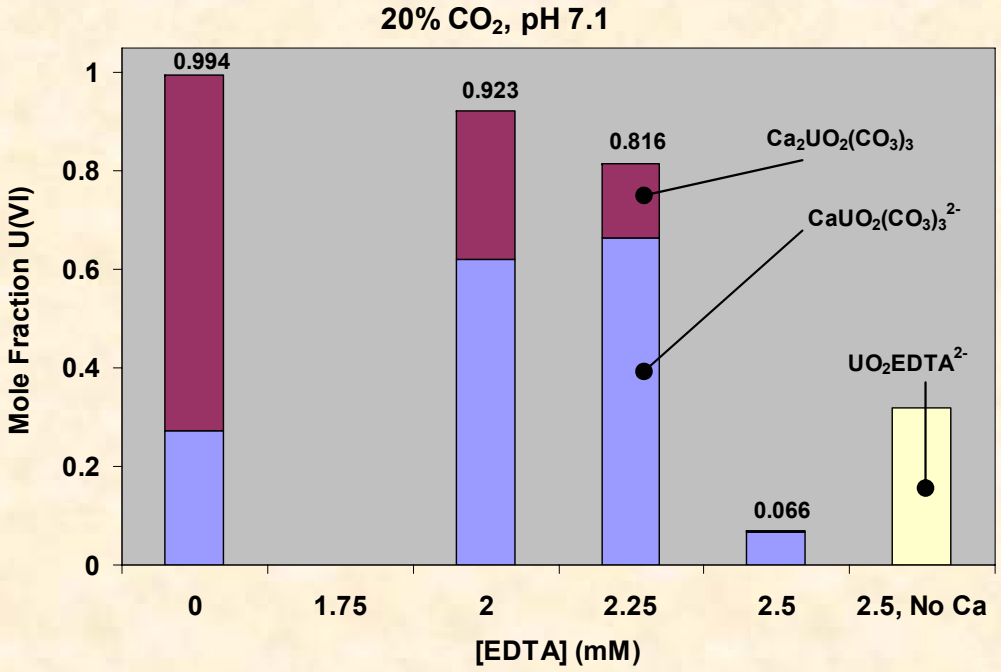
- **U-EXAFS : No U-U backscatter – indicates dissolved U, not nanoparticles that passed 0.2 µm pores in filter.**

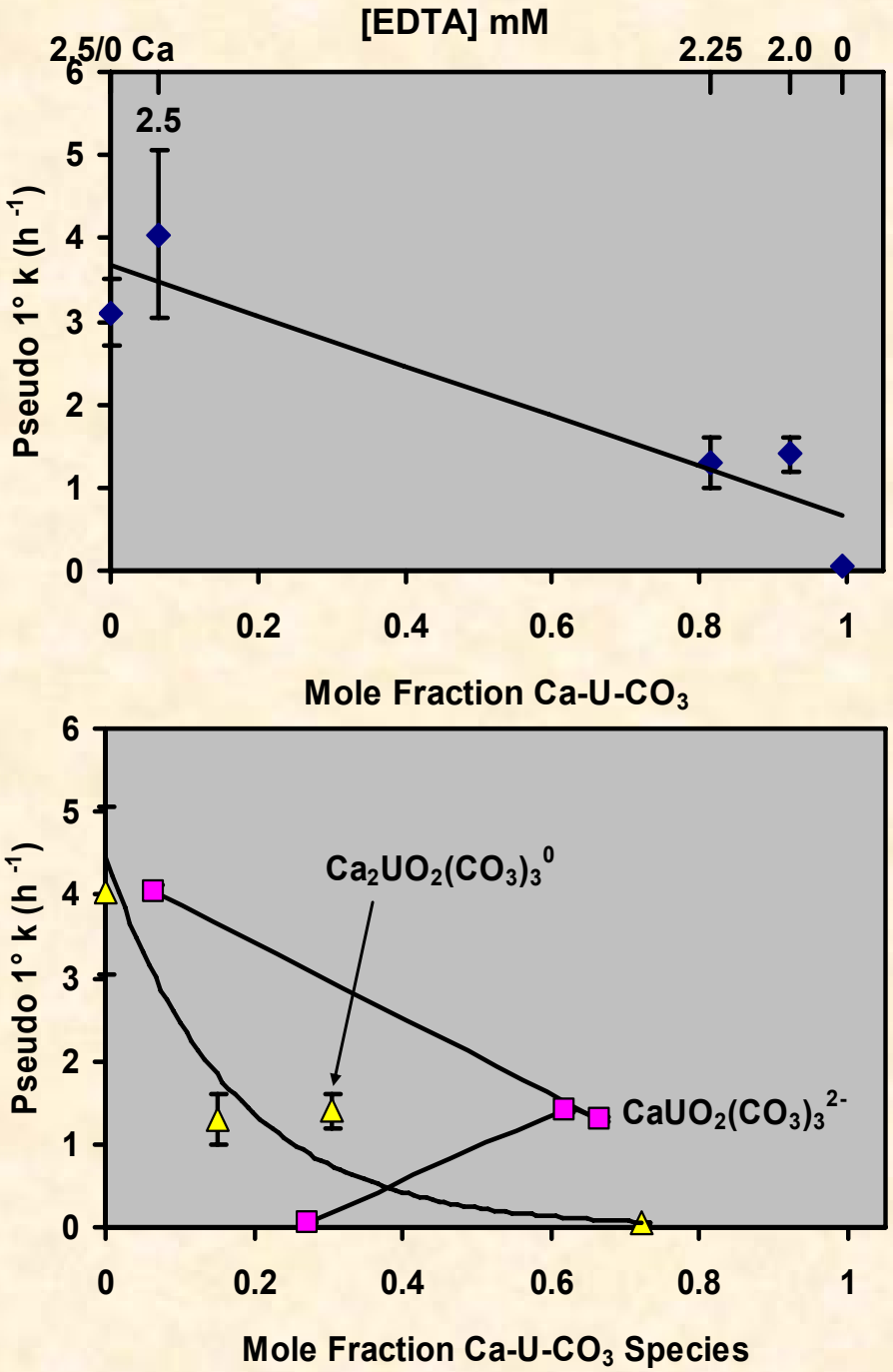
U(VI) speciation controlled by [EDTA] pH 6.5



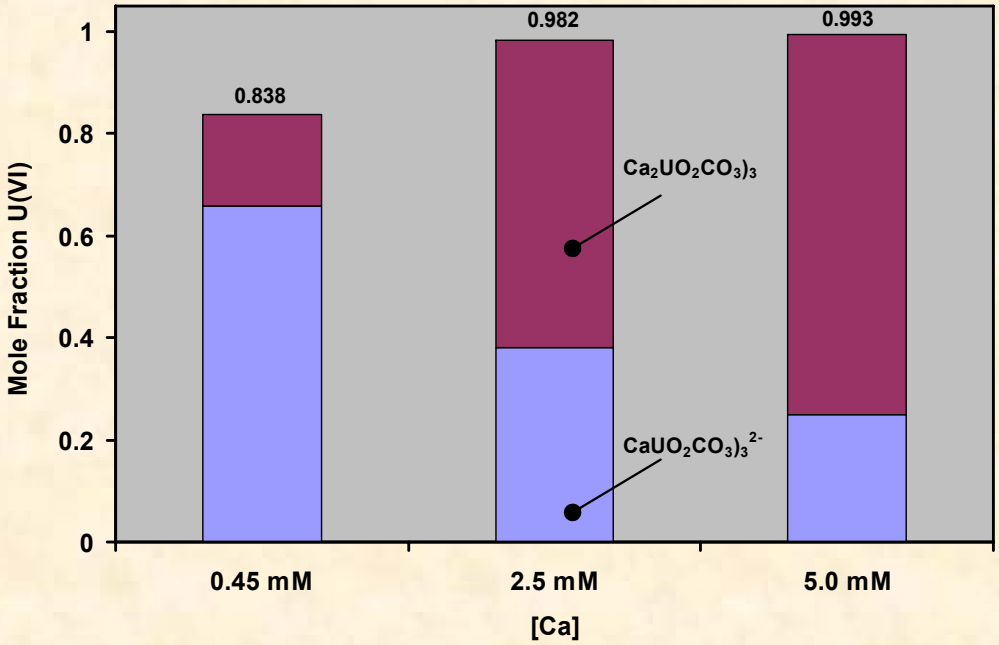


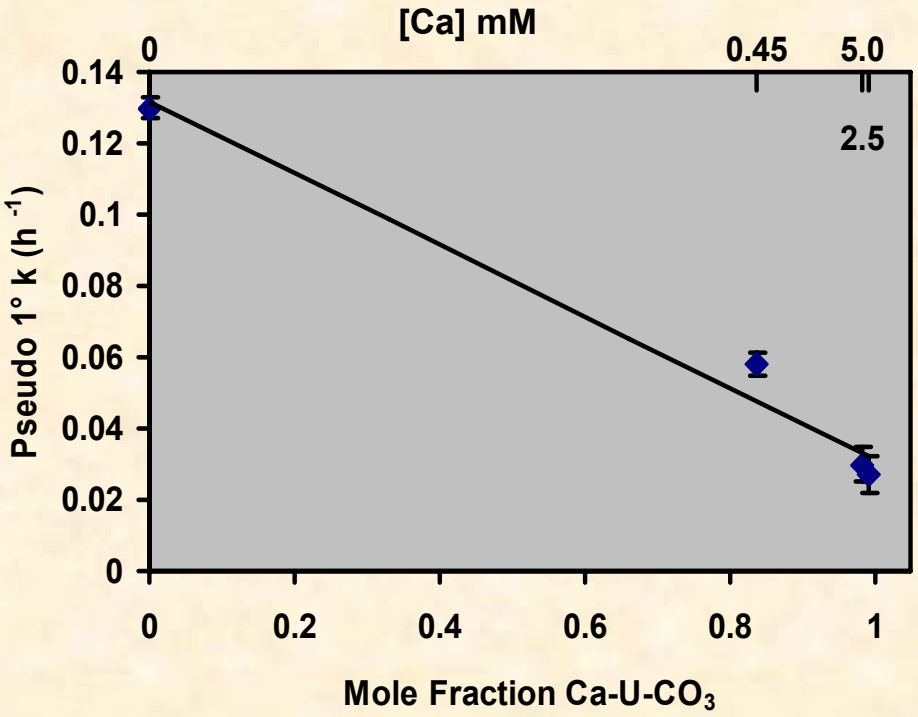
U(VI) speciation controlled by [EDTA] pH 7.1

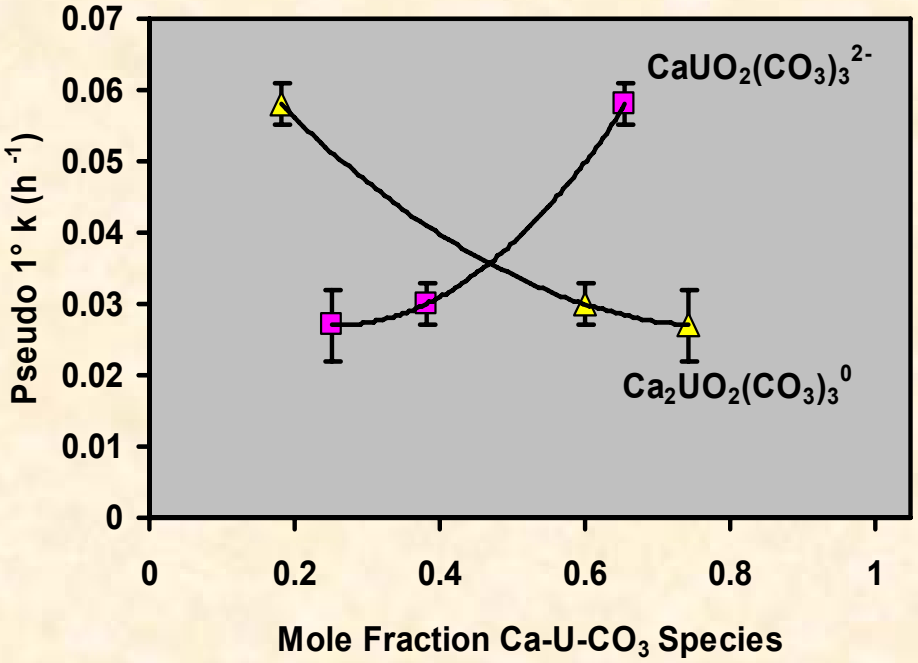




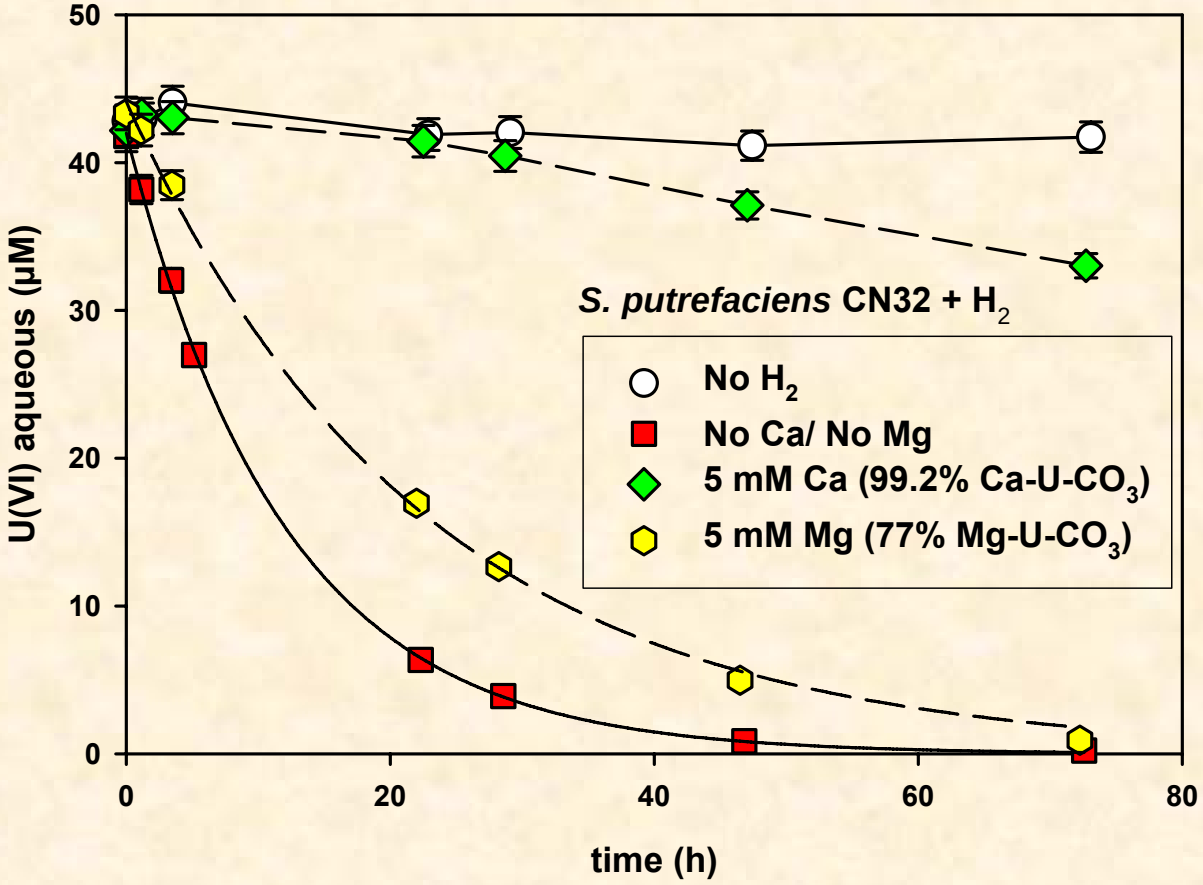
U(VI) speciation controlled by [Ca] pH 6.9







Effect of Mg on bacterial U(VI) reduction (preliminary):



- **Mg slows rate of U(VI) reduction**
  - **Effect weaker than Ca**
  - **Mg complex is weaker than the Ca complexes**
  - **The $MgUO_2(CO_3)_3^{2-}$ complex is dominant**

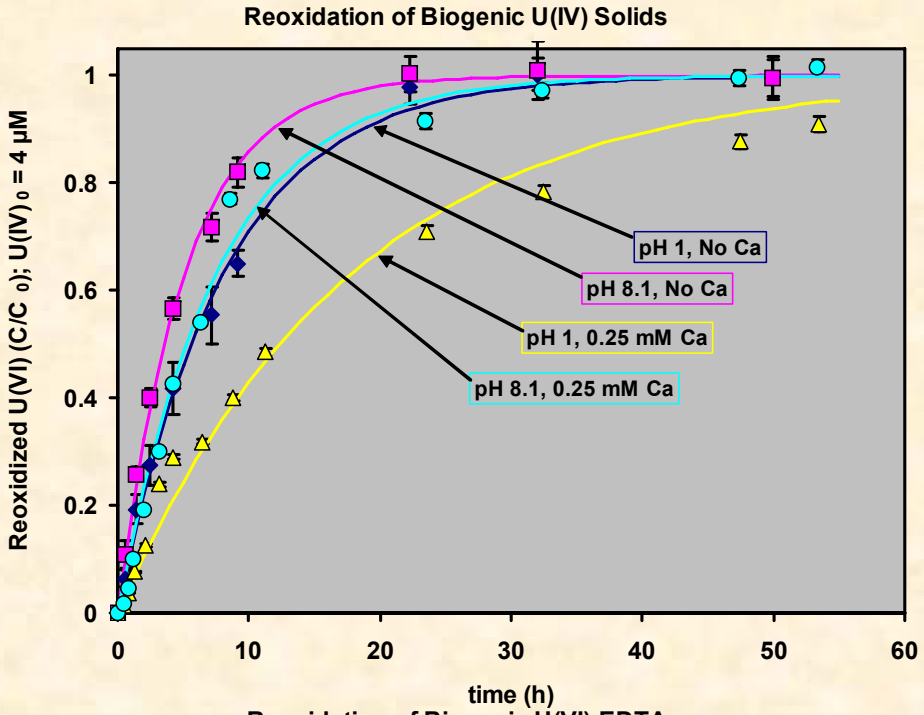
Summary 2:

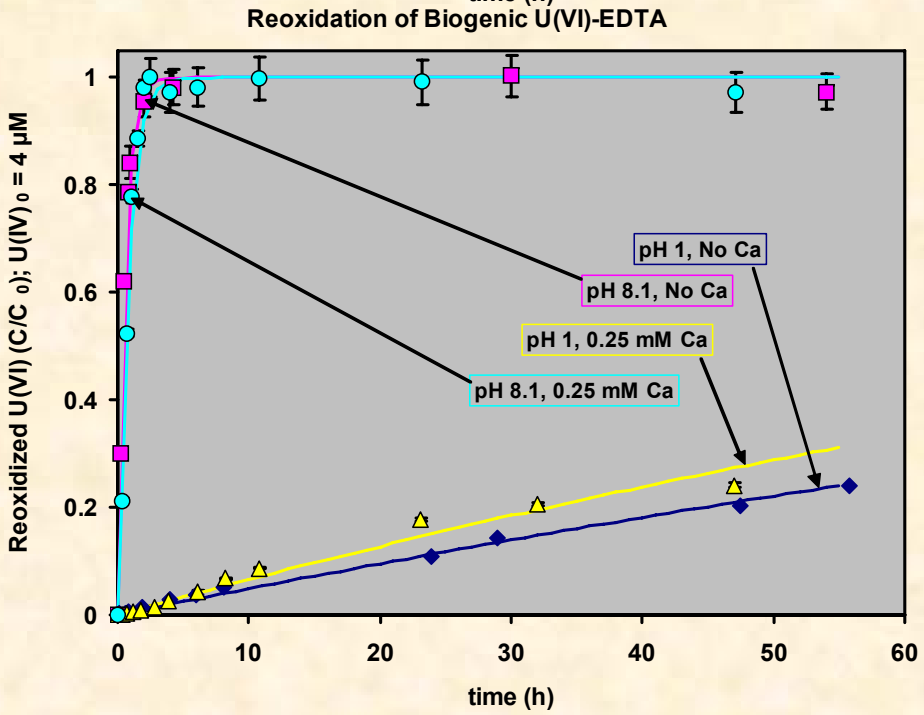
- **Rate and extent U(VI) bioreduction related predicted speciation.**
  - **Tentative evidence that the uncharged $Ca_2UO_2(CO_3)_3^0$ complex governs the observed rate.**
- **EDTA additions:**
  - **A stable U(IV)EDTA complex generated**
    - **Suggests that neither $UO_{2,am}$ nor Uraninite controlling U(IV) solubility.**
- **Nature of thermodynamic and kinetic constraints is not entirely clear:**
  - **Thermodynamic constraints do not seem to limit rate or extent U(VI) reduction**
    - **U(VI)EDTA weaker electron acceptor than the Ca-UO_2-CO_3 species yet is reduced faster and to a greater extent.**
  - **Analogous species exist for other alkaline earth elements**
    - **Impact on U(VI) bioreduction related to strength of complex**
- **Rate of complex dissociation?**

Reduced Product Stability: Effects of pH, EDTA, and Ca^{2+} on Biogenic U(IV) solids and U(IV)-EDTA Oxidation (Dong and Brooks, *in prep*)

- **Biogenic U(IV) samples prepared anaerobically.**
- **Removed from glovebox and exposed to atmosphere (21% O_2) without stirring/ shaking.**
- **U(VI) monitored over time.**

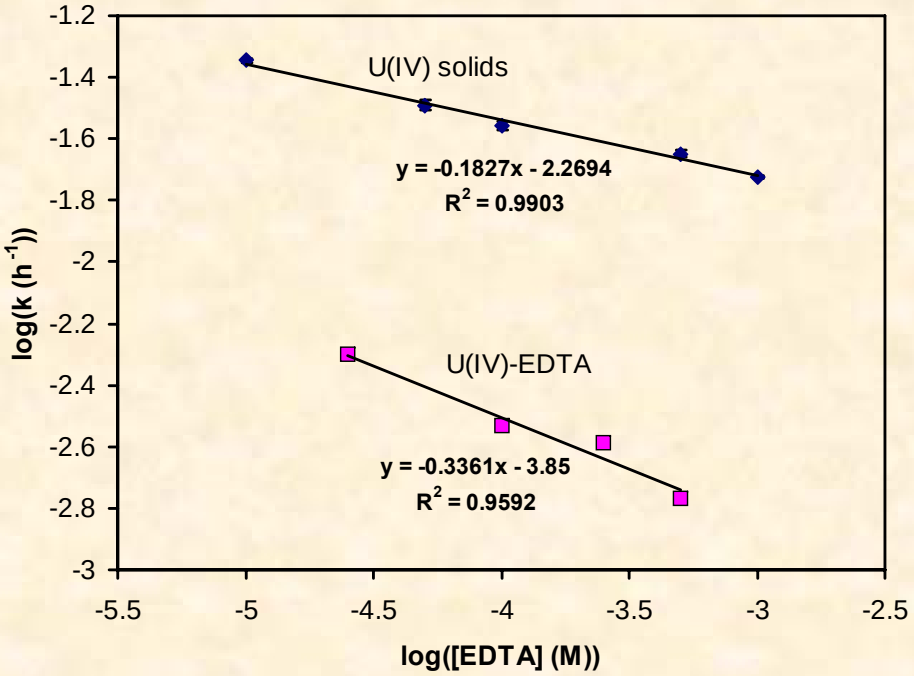
$$\frac{C(t)}{C(0)} = 1 - exp(-kt)$$



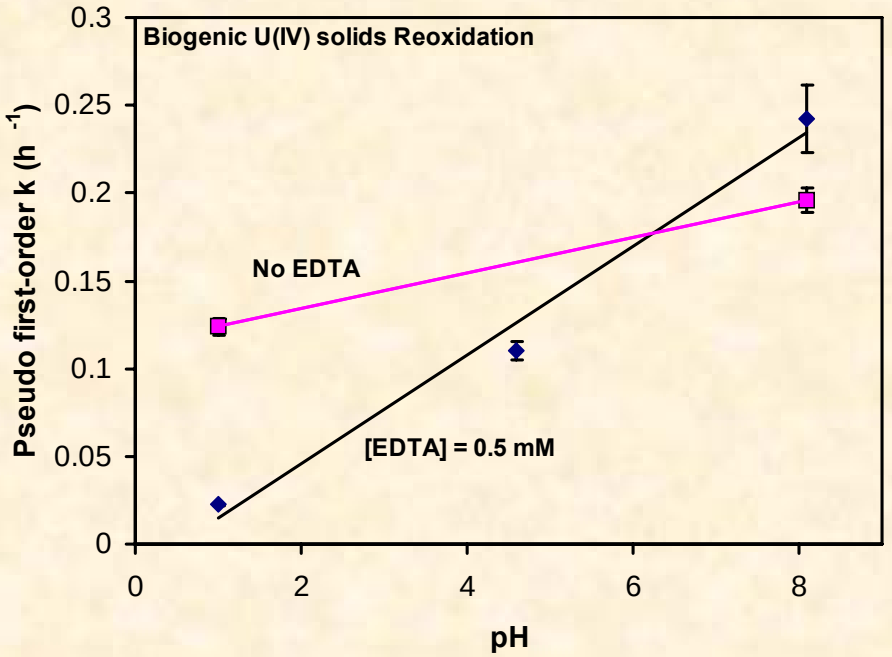


- **The oxidation rate of U(IV) solids and U(IV)-EDTA increased with increasing pH and decreasing [Ca]**

- **EDTA slows the rate of biogenic U(IV) oxidation at pH 1.**



- **EDTA enhances the rate of biogenic U(IV) solids oxidation as pH increases.**



Summary 3:

- **Biogenic U(IV) oxidation**
  - **Increased with pH**
  - **Decreased with addition of Ca**
- **At pH 1 EDTA decreased oxidation rate**
- **As pH increased, EDTA enhanced U(IV) oxidation rate.**
- **Improved method to determine U(IV) from difference (U_{TOT} – U(VI)) by stabilizing U(IV) in samples.**